ORIGINAL ARTICLE

Assessment of Daytime and Nighttime Ground Level Ozone Pollution in Malaysian Urban Areas

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ABSTRACT

Introduction: Ozone (O_3) is a significant component of photochemical smog as a typical secondary which is formed via nitrogen oxide photochemical interactions with volatile organic compounds (VOCs). This research discerns the complex influence of meteorological parameters and air pollutants influencing O_3 concentrations. **Methods:** Data were acquired from 1 January 2018 until 31 December 2020 that including ozone (O_3), nitrogen oxide (NOx), nitric oxide (NO), sulphur dioxide (SO_2), nitrogen dioxide (NO_2), carbon monoxide (CO), particulate matter (PM_{10}, $PM_{2.5}$), wind speed, solar radiation, temperature, and relative humidity (RH). Data were analysed using descriptive statistics in terms of line graphs. **Results:** The results demonstrate that the O_3 concentration peaked around 14:00 hours and dropped at night (20:00 hours) owing to the lack of sunshine and redox processes. **Conclusion:** In conclusion, ozone precursors played an important role in ozone formation and the findings of this research are valuable for policymakers and other interested parties.
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INTRODUCTION

Ozone is made when nitrogen oxides and volatile organic compounds in the air react with light to form ozone precursors (1). In specific, ozone (O_3) precursors were emitted from anthropogenic sources, and certain volatile organic compounds (VOCs) have emitted from plant-based biogenic materials (2). The rise in O_3 was responsible for morbidity and death in humans. Exceedances of O_3 concentrations lead to short-term air pollution exposure (a measure of morbidity) including Chronic Obstructive Pulmonary Disease (COPD), cough, shortness of breath, wheezing, asthma, respiratory diseases, and high hospitalization rates (3, 4). Moreover, long-term O_3 exposure has been linked to decreased lung function and impaired or aberrant lung development in children (5). Under the WHO ozone guideline requirements, the most vulnerable groups are examined, including those with established respiratory disorders such as asthma and COPD, children, older persons, and those who are active outside, particularly outdoor workers.

Meteorological factors played an important role in the variation of O_3 concentrations. Low temperature prevents convective diffusion of O_3 precursors, resulting in low O_3 concentrations. (6) and O_3 has a negative relationship with relative humidity. In contrast to the diurnal pattern of O_3, the diurnal trend of relative humidity shows high levels at midnight and early in the morning, gradually declining after sunrise (7). Wind promotes mixing and transport between the boundary layer and the higher free atmosphere, allowing trace pollution species to disperse along horizontal and vertical levels (8). In conditions of high air temperature, the primary contributors to the increasing ozone pollution may be the greater biogenic nitrogen oxides (NOX) and VOC emissions (9). High CO concentrations may drastically alter the atmosphere's oxidation capability (6). O_3 production is contingent on solar intensity, which is closely related to air temperature (9). Ironically, when the amount of soot

and other carbonaceous aerosols in the air from burning coal, diesel, and biomass decreases, the air gets clearer and the sun shines brighter, which makes it easier for O_3 to be formed (9). Particulate matter (PM) with an aerodynamic diameter of 2.5ηm or less may act as a sink for free radicals that contribute to O_3 production. Moreover, climatic factors including sunshine, cloud cover, and relative humidity have been shown to affect both NOX and VOC (10).

The community raised air quality as one of the main issues nowadays because of the negative effects that ambient ozone has on both the environment and the health of humans. O_3 precursors, NOx, and VOCs combine with sunlight to form tropospheric ozone (9). Premature mortality and a number of harmful health conditions, including cardiovascular disorders, are linked to ambient ozone exposure. The chemical coupling induces specific mechanisms for the understanding of the trend of ozone. In addition, this study referred to sustainable development goals (SDG), SDG-11 on sustainable cities and communities, and according to the World Health Organization (WHO) (11), almost 99% of the world's population lives in areas where air quality beyond the WHO standard, including excessive amounts of pollutants, and polluted air kills approximately 7 million people globally each year. This research discerns the complex influence of meteorological parameters and air pollutants influencing O_3 concentrations. Thus, this study is very important in providing information on the mechanisms of O_3 formation for the assessment of the impacts of ozone on human health and the environment through predictive modeling and risk assessments.

MATERIALS AND METHODS

Study areas and data acquisition

This study focused on three urban areas and a background area located in Keningau, Sabah. The background area represents the lowest ambient air pollution which also gazettes as a clean air area. Table I lists the station ID, site of the air quality surveillance station, and coordinate (latitude and longitude) for each chosen station. The secondary data in terms of 3 years' time span from 1st January 2018 until 31st December 2020 were used in this study. This long-term historical data is needed as it represents the variation of pollutants comprehensively [12]. Hourly data of air pollutants (O_3, SO_2, NO_2, NO, NOx, CO, PM_{10}, and $PM_{2.5}$) along with meteorological factors (wind speed, relative humidity, solar radiation, and temperature) were obtained from the Department of Environment (DOE). The data are not available for several periods of hours because of missing due to several reasons. An incomplete dataset affects the quality of data and imputations are needed before further analysis. The deletion technique was used in this study due to the number of missing values of more than 40% [6]. The deletion technique is suitable for missing data of more than 40% to avoid bias among the data. Then, the data set is used to analyze in terms of descriptive statistics, and inferential statistics.

Table I: Selected Study Areas

Site	Station ID	Location	Coordinate	Zone
S1	CA 0016	Sek. Men. Keb. Seri Permaisuri, Cheras	03° 06′ 22.44″ N 101° 43′ 04.50″ E	Urban
S2	CA 0044	Sek. Keb. Chabang Tiga, Kuala Terengganu	05° 18′ 29.13″ N 103° 07′ 13.41″ E	Urban
S3	CA0065	Depot Ubat Kementerian Kesihatan Malaysia, Kuching	01° 33′ 44.02″ N 110° 23′ 20.24″ E	Urban
S4	CA 0052	Sek. Men. Keb. Gunsanad, Keningau	05° 20′ 21.54″ N 116° 09′ 49.16″ E	Background

Data analysis

Equations 1 and 2 explain most of what happens when O_3, NO, and NO_2 change into each other in the atmosphere.

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{Equation 1}$$

$$NO_2 + (hv)\ (+O_2) \rightarrow NO+O_3 \quad \text{Equation 2}$$

As a whole, Equation 2 has the opposite effect of Equation 1, creating a cyclical situation without no net chemistry. These reactions make up a closed system that separates NOX into its constituent forms of NO and NO_2, as well as oxidant (OX) through its constituent forms of O_3 and NO_2, thereby maintaining the same overall mixing ratio of NOx and Ox (13). NO, NO_2 and O_3 often equilibrate within minutes throughout the day, a "photo stationary state" (14).

RESULTS

Due to rising solar radiation, automobile emissions, and high population increase made known by human activities including building, open burning, and mobile sources, the diurnal pattern of O_3 concentration exhibits maximum concentration at roughly 1400 hours (15). An increase in O_3 concentration and temperature from 0900 to 1300-1500 hours indicates that O_3 concentration and temperature are significantly connected (13). Based on Figure 1, the average ground level of O_3 concentration, the average temperature, and the average solar radiation have the same form of the multiple-line graph on an hourly basis. The reduction of NOx and VOCs leads to decreasing O_3 sensitivity to temperature (16). The high concentration of O_3 in the afternoon, between 1300 and 1500 hours, is related to the highest temperature and solar radiation occurring during this time (17). According to Silva et al. (18), the presence of solar radiation during the day, from 1000 to 1400 hours, causes an increase in O_3 concentration, whereas the absence of solar radiation during the night causes a decrease in O_3 concentration. The diurnal plot shows that night-time O_3 concentrations are relatively low and more consistent from 1900 to 0700 hours (18). The long-distance transport of NOx responding to sunlight and the photochemical interaction of O_3 precursors such

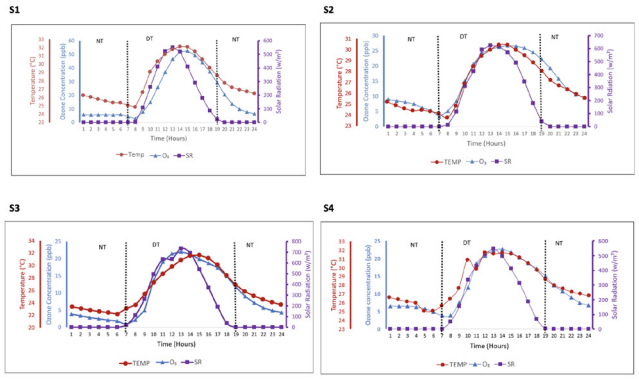

Figure 1: Average concentration of ground-level O_3, temperature, and solar radiation. O_3 concentration shows maximum concentration during the mid-day of around 1400 hours.

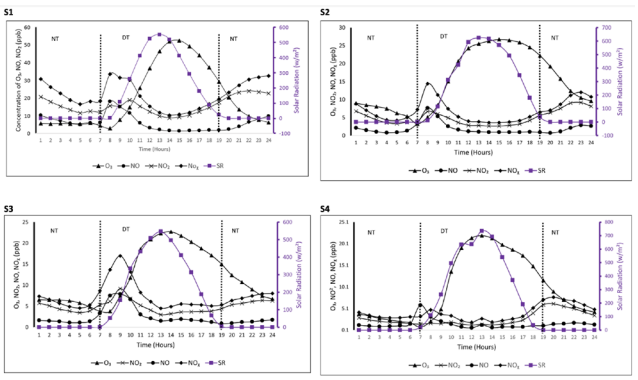

Figure 2: Average concentration of ground-level O_3, NO_2, NO, and NOX. The diurnal pattern of NO_2 shows two significant peaks in the morning from 0900 to 1000 hours and in the evening from 2000 to 2200 hours.

volatile organic compound (VOC) with the ambient atmosphere by natural resources may cause the O_3 concentration to peak around 1400 hours till 1500 hours and start to drop at night around 2000 hours (8). The O_3 content progressively declined towards dusk due to the absence of sunshine and redox processes, beginning at 16:00 hours and ending around 21:00 hours (19). Due to a lack of solar light, the O_3 concentration steadily drops until evening at 1600 hours and then continues to decline more gradually during the night at 2100 hours until morning at 0700 hours.

The diurnal fluctuations of the hourly average of O_3 and its predecessors, NO_2 and NO, are shown in Figure 2. These variations highlight the distinct properties of O_3 and its precursors. O_3 generation was photochemically produced, and the diurnal pattern of O_3 concentrations exhibited an increasing tendency after dawn, peaking at approximate midday, and declining in the afternoon. This trend continued throughout the 24-hour period (9). NOX is the most important role in the formation and destruction of O_3 concentration in the troposphere (7). The lowest O_3 production was observed in the morning around 0700 hours. The daily pattern shows that from 1900 to 0700 hours, nocturnal O_3 concentrations declined considerably (20). According to Figure 2, the diurnal pattern of NO_2 exhibits two distinct peaks in the morning between 0900 and 1000 hours and in the evening between 2000 and 2200 hours, with the second peak being smaller owing to emission intensity and existing climatic conditions (21). According to Ismail et al. (13), the high of NO_2 in the morning comes around two hours after the peak of NO in the morning, which happens at 0800 hours, whereas the peak of O_3 happens at 1400 hours. It appears 6 to 8 hours after NO_2 peaks at 1000 hours and NO at 0800 hours. NO begins to decline after the morning peak at 0800 hours, reaching a lower value between 1300 and 1400 hours. It was discovered that reductions in NO and NO_2 coincide with increases in O_3 (22).

The variation of the value of J2/ K1 over time at Cheras, Kuala Terengganu, Kuching, and Keningau of NO, NO_2, and O_3 is shown in Figure 3 which the maximum value reached at around 1500 hours. This adequately describes daily averaged data, which is associated with the chemical coupling among those species getting governed by the reactions of Equations 1 and 2. Figure 4(a) depicts the variance in the mean concentration of oxidant (OX) (O_3 and NO_2). Ox concentration peaks during midday and declines at night, similar to O_3 concentration (13). Owing to photochemical O_3 production, the Ox concentration increases steadily after dawn, peaks throughout the day, and then drops gradually till the next morning (9). Figure 4(b) depicts the change in the ratio of NO_2 to Ox. As a result of the greater concentration of O_3 during the day, the ratio of NO_2 to Ox is lower than normal. This variation in NO_2 and O_3 portioning may be due to the speed at which chemical reactions occur or the amount of time that exists for them to do so. Due to the reduced O_3 concentration throughout the day, the $[NO_2]/[Ox]$ ratio rose (23).

The concentrations of sulphur dioxide (SO_2), carbon monoxide (CO), nitrogen dioxide (NO_2), and particulate matter (PM_{10} and $PM_{2.5}$) fluctuate with a similar tendency, as shown in Figure 5. The initial concentrations of CO, NO_2, PM_{10}, and $PM_{2.5}$ are starting increase at 0700 hours and peaked around 0800 hours

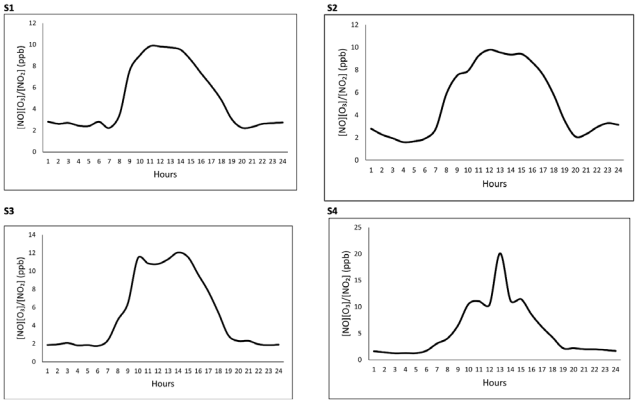

Figure 3: Variation of Average Value of J_2/K_1. The variation of the value of J_2/K_1 over time reached the maximum value that occurred at 1500 hours.

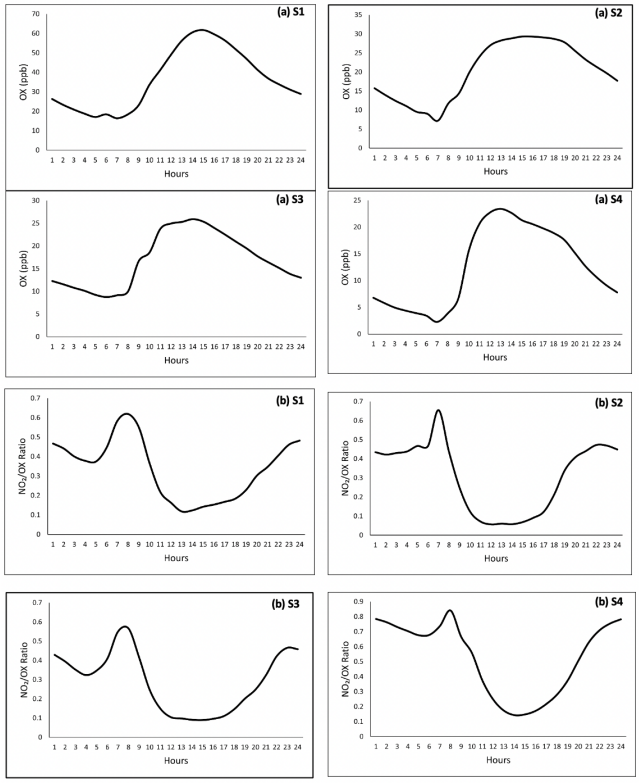

Figure 4: (a) Variation of Mean values of OX, (b) Variation of Average Values of NO_2/OX Ratio. OX concentration shows a mid-day peak and drops at night. A smaller ratio of [NO_2]/[OX] is due to the higher concentration of O3 during the day.

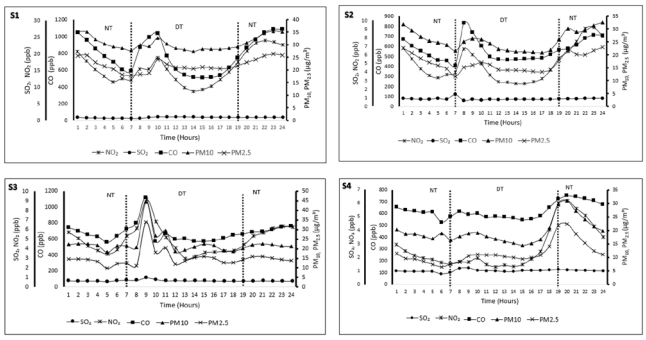

Figure 5: Average concentration of SO_2, CO, NO_2, PM_{10}, $PM_{2.5}$. The concentration of sulfur dioxide (SO_2), carbon monoxide (CO), nitrogen dioxide (NO_2), and particulate matter (PM_{10} and PM2.5) changes with a similar tendency.

until 1000 hours. It might be caused to a variety of factors, including local pollutants from transportation and open burning (24). During the morning, the level of the particulate matter reached its peak between the hours of 0800 and 1000, which coincided with the rise in CO and NO_2 concentrations. Subsequently, a spontaneous decrement in the particulate matter was recorded between the hours of 1200 and 1800, which was also recorded concurrently with the decrease in both parameters (21). Similar patterns were seen for the evening peak of particulate matter around 1900 hours, which coincided with increases in CO and NO_2, and the abrupt reduction in the particulate matter after 2000 hours, which was associated with falls in CO and NO_2 (12, 21, 24). Meanwhile, the concentration of SO_2 remains constant during daytime and night-time at Site 1 but there exists increasing of SO_2 concentration from around 0700 hours until 0900 hours (Site 2, Site 3, and Site 4), and decreasing at around 1000 hours and then remain constant during the night-time. SO_2 has a short lifetime and can rapidly convert to sulfate (SO4) by oxidation and contact with particles and water vapor (21). Low concentrations of SO_2 suggests that traffic-related emissions have little influence on SO_2 variations. Hence, the sources of sulphur dioxide are not directly connected to exhausts from vehicles; rather, it is possible that they are attributable to emissions from industries (21, 24). The concentration of CO, NO_2, PM_{10}, and $PM_{2.5}$ at Site 1, Site 2, and Site 4 are starting decrease around 1100 hours and increased during night-time at 1900 hours because the freight vehicles can only travel at specific times throughout the night and the emission factor of freight vehicles, such as high-tonnage diesel trucks, is substantially higher than that of conventional motor vehicles. The late-evening peak might also be attributed to meteorological factors, notably air stability and wind speed (25). Particulate matter concentrations were marginally higher at night between 2000 and 2300 hours due to particle accumulation caused by inversion circumstances (21). These impacts are also strongly connected to CO and NO_2 gaseous emissions from vehicle exhaust (24). When traffic emissions started to rise in the evening, people were told that the amount of NO_2 and particulate matter was going up. Particulate matter is significantly affected by nitrogen dioxides due to their oxidation in the atmosphere to aerosol nitrate and the production of CO from the oxidation of VOCs (21). The amounts and constituents of nitrate aerosols are determined, in large part, by the precursor emissions, that are nearly entirely of human origin.

The fluctuations in wind speed, relative humidity, and temperature that occur during the day are shown in Figure 6, along with the properties that are unique to each variable. The average wind speed, relative humidity, and temperature starting increase at 0700 hours and slowly decrease at 1900 hours. There is a fluctuation on the average wind speed, relative humidity, and temperature which occurs between 0800 hours and 1800 hours. The high average wind speed during daytime is due to the dispersion of pollutants in the atmosphere as well as the emission from the transport of dust particles (26). Warm air can contain more water vapor than cold air, therefore daytime humidity is lower than nocturnal humidity, which might approach 100% relative humidity (21).

DISCUSSION

Suryati et al. (27) and Abdullah et al. (28) found high O_3 concentrations during the mid-day owing to the interaction of ozone precursors with the presence of sunlight, which may originate from anthropogenic sectors and vehicular transporting raw materials for the

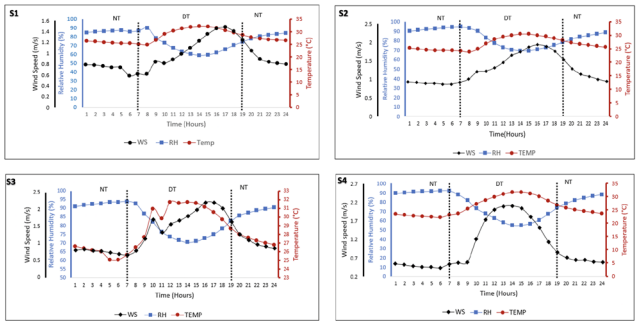

Figure 6: Average wind speed, relative humidity, and temperature. The average wind speed, relative humidity, and temperature starting increase at 0700 hours and slowly decrease at 1900 hours.

industrial production process. These studies supported the increased trends of ozone concentrations. The absence of solar radiation causes the O_3 concentrations to decline continuously until nightfall, after which they continue to decline at a slower rate throughout the night, resulting in levels that are consistently low (29). The higher solar radiation intensity during the daytime may lead to favorable conditions for powering photochemical reactions (30). Hou et al. (31) found that the temperature inversion held daytime pollutants such as nitrogen monoxide and NO_2, raising nitrogen oxides at night. During the night-time, the O_3 concentration was far lower than the day-time concentration due to the absence of photochemical reactions (14). The O_3 concentration was decreased lower in the morning until the incoming solar radiation appeared to produce O_3 (32). The lack of photochemical processes that transform O_3 precursors into O_3 is principally responsible for the low concentrations. Chemical loss at night due to NO titration and deposition may reduce O_3 concentrations (14). In addition, the nighttime decrease in O_3 concentrations is attributable to the interactions between O_3 and NO_2, which create dinitrogen pentoxide (N2O5) and nitric acid (NHO_3) (33). This phenomenon may have some connection to the intense sun radiation that is there, which is known to encourage the production of O_3 (10). Since photochemical processes that turn O_3 precursors into O_3 aren't happening at night, the concentration of O_3 is quite low and stays relatively steady throughout those hours (19). Chemical loss through NO titration and deposition may also diminish O_3 concentrations at night (19). Similarly, Wang et al. (34) revealed that the usual diurnal trends of NO concentrations are similar to those of NO_2, with relatively high concentrations seen at night and peak concentrations associated to vehicular emission in the morning. The lack of sunlight causes the creation of ozone to halt, which in turn boosts the effectiveness of the process that removes pollutants from the atmosphere by reducing their concentration. The decrease in O_3 concentration may be attributed to the increase in NO_2 concentration. NO is a main contaminant, while O_3 and a significant portion of NO_2 are secondary pollutants generated by a series of complicated reactions. As shown in Equation 1, NO is transformed to NO_2 through a reaction with O_3. Photolysis converts NO_2 back to NO throughout the day, resulting in the regeneration of O_3 (23) as shown in Equation 2. The presence of the vertical mixing layer had an effect, as well, on the concentrations of the air pollution. During the day, pollutants would be diluted as the mixing layer rises, and at night, pollutants would be contained inside the nighttime planetary boundary layer (NPBL) (13). This inversion traps emitted pollutants including NO and NO_2, which causes the hourly NOX concentration to increase at night (34). The concentrations of NO, NO_2, and O_3 are connected by the use of the phrase [NO]. $[O_3] / [NO_2] = J_2/K$, where J_2 is the rate of NO_2 photolysis and K1 is the rate coefficient for the interaction of NO with O_3, and where J_2 is the rate of NO_2 photolysis (13).

CONCLUSION

In conclusion, the diurnal cycle of O_3 concentration has a mid-day peak (1400 hours) due to the increasing of solar radiation, emission from vehicles and high population growth notified through human activities. Meanwhile, the O_3 concentration gradually decreased slowly towards the evening, starting 1600 hours, and ending 2100 hours due to the temperature inversion and absence of photochemical reactions. Besides, the O_3 concentration and its precursors (NO_2 and NO) illustrate their characteristics. The morning peak of NO_2 occurs about two hours after the morning peak of NO at 0800 hours while O_3 peak at 1400 hours. It appears 6 to 8 hours after NO_2 peaks at 1000 hours and NO at 0800 hours but NO begins decline after morning (0800 hours) and reaching a lower value between 1300 to 1400 hours. It's found that, both NO and NO_2 decreases correlate with an increase O_3. There is chemical coupling occurs between O_3, NO_2 and NO. These reactions constitute a close system that partitions NOX into its component forms of NO, NO_2 and OX into its component forms of O_3 and NO_2, while leaving the total mixing ratio of both NOX and OX unaltered. The concentration of SO_2, CO, NO_2, PM_{10} and $PM_{2.5}$ are changes with the similarity tendency. This study shows that the secondary pollutants such as O_3 concentrations are complex in their formation, relying on many factors including the ozone precursors, air pollutants, and meteorological factors. The projection of O_3 in the future must be based on the nonlinear modeling approach which can capture the complexity of O_3 in nature for impact analysis toward humans and the environment.

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